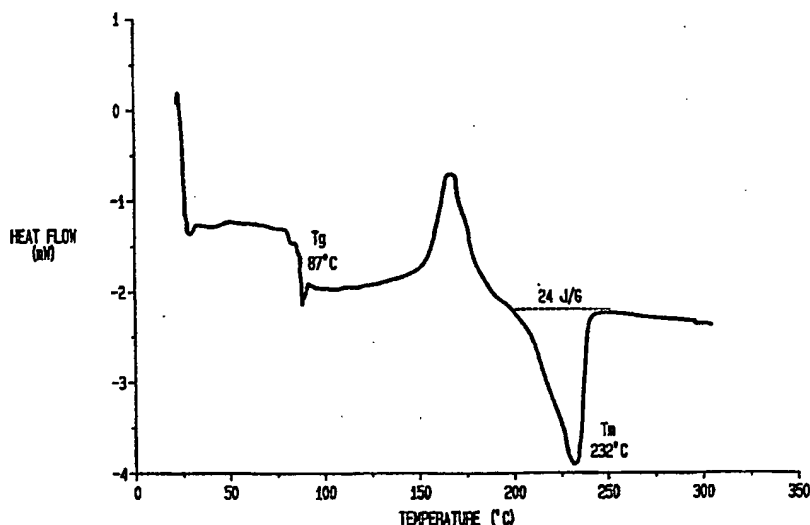




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B29C 49/00, 67/24, C08L 67/02		A1	(11) International Publication Number: WO 96/35571
			(43) International Publication Date: 14 November 1996 (14.11.96)
(21) International Application Number: PCT/US96/03414 (22) International Filing Date: 13 March 1996 (13.03.96) (30) Priority Data: 08/437,826 9 May 1995 (09.05.95) US (71) Applicant: HOECHST CELANESE CORPORATION [US/US]; Route 202-206, Somerville, NJ 08876 (US). (72) Inventors: CHEN, Paul, N. Sr.; 188 Gates Avenue, Gillette, NJ 07933 (US). MUSIC, Kenith, P.; 28 New Jersey Avenue, Flemington, NJ 08822 (US). McNEELY, Gerald, W.; 707 Meadowbrook Drive, Spartanburg, SC 29307 (US). (74) Agents: FERRELL, Michael, W.; Hoechst Celanese Corpora- tion, Patent Dept., 86 Morris Avenue, Summit, NJ 07901 (US) et al.		(81) Designated States: JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.	

(54) Title: TRANSESTERIFIED PET/PEN VIA MELT EXTRUSION



(57) Abstract

A process for making a transparent blow molded product made of a copolyester of PET and PEN that does not thermally deform at temperatures up to 85-87 °C, and the product of that process, especially a transparent blow molded bottle. The copolyester is made by transesterifying a 20/80 (w/w) PEN/PET via melt extrusion at a temperature of from about 250 °C to about 290 °C for a time sufficient to produce about 1-20 % transesterification of said polymers, forming a copolymer. The copolyester is then injection molded at a temperature of from 290 °C to about 320 °C to form a transparent preform in which the copolymer has a glass transition temperature of about 85 °C or higher and a melting point temperature of at least about 225 °C. The copolymer is then thermo-stretch blow molded to form a transparent product.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

TRANSESTERIFIED PET/PEN VIA MELT EXTRUSION

Background of the Invention

This invention relates to copolymers of poly(ethylene terephthalate) ("PET") and poly(ethylene naphthalene 2,6-dicarboxylate) ("PEN") and processes for making these copolymers by transesterifying PET and PEN, especially via melt extrusion.

PET is a very common material for packaging applications due to its good barrier properties, relative low cost and weight, toughness, and ability to form transparent films, bottles, and other packaging materials. For example, PET is widely used for making bottles for soft drinks, providing a lightweight alternative to glass.

To enhance the barrier properties, it is desirable for the polymer to have some amount of crystallinity; crystalline polymers generally have better barrier properties (e.g., lower oxygen permeability) than amorphous polymers. Crystallinity also enhances the strength and washability of polymers. At the same time, transparency is commercially desirable in many applications. Common PET blow molded soft drink bottles are transparent, but have sufficient crystalline character to enhance barrier properties, strength and washability. Such a polymer exhibits a glass transition temperature (" T_g ") due to its amorphous phase as well as a melting point (" T_m ") at a higher temperature due to its crystalline phase. The T_g places a practical upper limit on use temperatures.

One drawback of PET is its relatively low glass transition temperature of about 75-78°C, which limits the temperature at which a PET bottle can be filled with liquid without deforming. Therefore, for liquids that are bottled hot, glass and metal containers are often used where PET is unsuitable.

Compared to PET, PEN has a higher glass transition temperature (about 119-124°C) and superior barrier properties, e.g., lower permeability to oxygen. PEN would be a very useful material for bottling applications, including hot liquid

bottling; unfortunately, the price of PEN is not competitive with alternative bottling materials.

Blends and copolymers of PEN and PET have been made in an attempt to provide a material that is cheaper than PEN but has a higher glass transition temperature and better barrier properties than PET. Unfortunately, a cost-competitive PET/PEN material having a sufficiently high glass transition temperature for hot fill applications has not been reported.

Shepherd et al. (5,006,613) described a tricomponent blend of PET, PEN, and a compatibilizing amount of a copolyester that produced transparent packaging suitable for hot fill applications.

McNeely et al. (U.S. Pat. No. 5,250,333) describes a modified PET in which alkoxylated polyol is incorporated. Units derived from 2,6-naphthalenecarboxylic acid may be incorporated for hot fill applications.

In two articles entitled, "TRANSESTERIFICATION OF POLY(ETHYLENENAPHTHALENE 2,6-DICARBOXYLATE)/POLY-(ETHYLENE TEREPHTHALATE) BLENDS", *ANTEC '93*, pp. 1222-27 (1993), and Reactive processing of poly(ethylene 2,6-naphthalene dicarboxylate)/poly-(ethylene terephthalate) blends, *POLYMER*, 1993, Vol. 34, No. 19, pp. 4060-4067, Stewart et al. describe blends of PET (containing varying amounts of catalyst(s)) and PEN made by melt mixing the polymers in an extruder at temperatures from 548-588 K (275-315°C) to produce varying amounts of transesterification. The PEN content of these blends was 80%, 65%, and 50%. It was reported that the degree of transesterification increased as the melt mixing temperature increased, and also as the melt mixing time increased. Stewart et al. further reported that the T_g increased as PEN content increased.

In an anonymous article numbered 28340 in *RESEARCH DISCLOSURE*, November 1987, melt blends of PEN and PET were disclosed, especially 25%,

50%, and 75% PET blends. The data in that reference suggests that the T_g for a 20/80 PEN/PET blend is well below 85°C.

Summary of the Invention

5 The present invention is a process for making a transparent blow molded product made of a copolyester that does not thermally deform at temperatures up to at least 85°C, said process comprising:

 melt extruding about four parts by weight poly(ethylene terephthalate) together with one part by weight poly(ethylene naphthalene 2,6-dicarboxylate) at a
10 temperature of from about 250°C to about 290°C for a time sufficient to produce about 1-20% transesterification of said polymers as measured by NMR (nuclear magnetic resonance spectroscopy), forming a copolymer;

 injection molding said copolymer at a temperature of from 290°C to about 320°C for three minutes or less to form a transparent preform in which said
15 copolymer has a glass transition temperature of about 85°C or higher and a melting point above about 225°C;

 thermo-stretch blow molding said preform at a temperature between said glass transition temperature and the crystallization temperature of the copolymer to form a transparent polyester product having a glass transition temperature of at
20 least 85 C, a melting point of at least 225 C, and a heat of fusion of at least 20 J/g as measured by DSC (differential scanning calorimetry).

The present invention also includes the product of said process.

 It is an object of the present invention to provide a transparent blow molded product, such as a bottle, made of a copolymer having a glass transition
25 temperature of at least 85-87°C that is formed by transesterifying a blend of 80% PET and 20% PEN by weight.

It is also an object of the present invention to provide a relatively inexpensive, transparent polyester bottle having good barrier properties that is suitable for hot fill applications.

5 It is a further object of the present invention to provide a process for making a transparent bottle or other blow molded product made of a copolymer, having a glass transition temperature of at least 85-87°C and a heat of fusion of at least about 20 J/g, that is formed by transesterifying a blend of 80% PET and 20% PEN by weight.

10 It is another object of the present invention to provide a process for transesterifying a blend of 80% PET and 20% PEN by weight to a level of 1-20% transesterification to form a block copolymer, as measured by NMR, and blow molding the copolymer to form a transparent, partly crystalline container or other object that does not thermally deform at temperatures below 85°C.

15 Other objects and advantages of the present invention will be apparent to those skilled in the art from the following description and the appended claims.

Brief Description of the Drawings

FIG. 1 shows the results of a DSC analysis of PEN used in the present invention.

20 FIG. 2 shows the results of a DSC analysis of PET used in the present invention.

FIG. 3 shows the results of a DSC analysis of a random 20/80 weight % PEN/PET.

25 FIG. 4 shows the results of a DSC analysis of a preform made according to the present invention.

FIG. 5 shows the results of a DSC analysis of the neck of a blow molded bottle made according to the present invention.

FIG. 6 shows the results of a DSC analysis of the bottom portion of a blow molded bottle made according to the present invention.

FIG. 7 shows the results of three consecutive DSC analyses of a particular 20/80 PEN/PET copolymer made according to the present invention.

FIG. 8 shows the results of the DSC analysis of each of two 20/80 PEN/PET copolymers made under different conditions.

Detailed Description of the Preferred Embodiments

In one preferred embodiment of the present invention, PET and PEN are melt extruded together in a PEN:PET weight ratio of 20:80 using a twin screw extruder at temperatures in the approximate range of 250-290°C, preferably 250-280°C, and most preferably 265-275°C, to form opaque pellets. The polymers must be heated in the extruder at such temperatures for a time sufficient to produce a low degree of transesterification, i.e., 1-20% transesterification and preferably no more than 15%.

This produces an opaque copolymer having a T_g that is about 85-87°C, and having a degree of crystallinity reflected by the existence of a T_m and a heat of fusion of at least about 20 Joules/gram ("J/g"). At this stage, it is preferred that the copolymer have two melting points in the range of 240-270°C, approximately corresponding to the melting points of PET and PEN, and a heat of fusion greater than 30 J/g. This copolymer is believed to comprise alternating blocks or strings of PET and PEN units; such a copolymer is commonly referred to as a block copolymer.

The extrusion speed or polymer throughput rate is inversely proportional to the residence time of the polymers in the extruder. If the speed is relatively low and the temperature is relatively high a greater degree of transesterification will occur, resulting in a more random copolymer having a lower degree of crystallinity, whereas a lower extrusion temperature and faster speed will cause less

transesterification and thus less randomness in the copolymer. Extrusion can be carried out temperatures somewhat higher than 290°C if the extruder residence time is shortened sufficiently to prevent over-transesterification; however, temperatures in the range of 250-280°C are preferable.

5 The percent transesterification of PEN/PET copolymers set forth herein is measured according to the method described by Stewart, et al., in *POLYMER*, 1993, Vol. 34, No. 19, pp. 4060-4067. In general, a sample of the copolymer is dissolved in a solvent mixture of 70/30 wt % deuterated chloroform and trifluoroacetic acid by weight. A proton nuclear magnetic resonance ("NMR")
10 spectrum of this copolymer solution is made. The NMR spectrum contains peaks that indicate the nuclear environment of the hydrogen atoms in the ethylene glycol monomer unit ("EG"), which differs depending on whether the EG is bonded to two terephthalate units ("T"), two naphthalate units ("N"), or one T and one N. A different peak corresponds to each of the three possible monomer unit sequences,
15 i.e. the sequences T-EG-T, T-EG-N or N-EG-N. Transesterification produces the T-EG-N sequence, so the size of this peak indicates the degree or percentage of transesterification; for 0% transesterification, there is no peak for the T-EG-N sequence. A random copolymer is 100% transesterified. The transesterification percentage is calculated by comparing the relative areas of the three peaks to that
20 of a theoretical random copolymer of the same overall composition to arrive at a mole percent transesterification.

 A random 20/80 PEN/PET copolymer has a significantly lower melting point, i.e. about 212°C, and a much lower heat of fusion (lower crystalline character), i.e. about 6 J/g, than the block copolymer produced in the process of
25 this invention. Such a copolymer does not exhibit the high barrier properties (e.g., low oxygen permeability) or the strength of the block copolymer described herein. Therefore, it is important to carefully control the amount of transesterification of the copolymer.

The degree of transesterification of the copolymer can be controlled by selecting an appropriate combination of extrusion temperature and time. One skilled in the art will readily be able to select suitable temperature-time combinations to achieve the desired level of transesterification based on the description and examples provided herein.

The melt extruded copolymer is then injection molded to form a preform at a temperature of about 290-320°C, preferably about 300-310°C, for no more than about three minutes, preferably one minute or less. The time and temperature must be limited because excessive heating at this stage could undesirably increase the amount of transesterification.

The injection molded preform of the present invention has a T_g of at least 85°C, typically about 85-87°C, is transparent to visible light, and has a T_m above 225°C; typically, the T_m is about 230-240°C.

The preform is thermo-stretch blow molded at a temperature in the range between the T_g and the crystallization temperature of the copolymer, typically in the approximate range of 100-140°C, preferably in the approximate range of 100-120°C. The temperature must be above the T_g so that the copolymer will flow and stretch, but must be below the temperature at which additional crystallization of the copolymer (the crystallization temperature) will occur to avoid introducing haziness into the material.

This process turns the preform into the final blow molded article, e.g., a bottle. The article is: transparent to visible light; exhibits a T_g of at least 85°C, preferably 87°C; has a T_m of at least 225°C, preferably at least about 230°C; and has a heat of fusion as measured by DSC of at least 20-30 J/g. The heat of fusion reflects the fact that the block copolymer of this invention is at least 3-4 times more crystalline than a random copolymer of 20/80 PEN/PET; preferably, it is more than 4 times more crystalline. This product will exhibit superior barrier properties

compared to PET products, suitable for packaging or bottling applications, and can be filled at higher temperatures than PET products because it has a higher T_g .

The following non-limiting examples illustrate several specific embodiments of the present invention.

5

EXAMPLE I

A total of 110 pounds of a blend of 20% PEN and 80% PET by weight were compounded at 275 C and a screw speed of 40 rpm in a Brabender PL2000 conical twin screw extruder. The measured inherent viscosity, T_g , and T_m of the polymers were: 0.6, 119°C, and 269°C for PEN (see FIG. 1); and, 0.9, 75°C, and 245°C for PET (see FIG. 2).

10

The blend material extruded and pelletized well. 100 pounds of good quality opaque pellets were produced. These pellets were dried at 120°C for 16 hours in preparation for molding.

15

EXAMPLE II

The procedure of Example I was followed again except that the extrusion was carried out at 290°C. The result was 100 pounds of good quality opaque pellets. These pellets were dried at 120°C for 16 hours in preparation for molding.

20

EXAMPLE III

The procedure of Example I was followed again except that the extrusion was carried out at 260°C. The result was 100 pounds of good quality opaque pellets. These pellets were dried at 120°C for 16 hours in preparation for molding.

25

COMPARATIVE EXAMPLE I

The procedure of Example I was carried out at 310°C and 20 rpm on 45 pounds of blend material, resulting in 40 pounds of clear pellets having non-uniform quality.

5

COMPARATIVE EXAMPLE II

A random 20/80 (w/w) PEN/PET copolymer was synthesized from the monomers ethylene glycol, terephthalic acid, and dimethyl-2,6-naphthalene dicarboxylate. The copolymer had very low crystallinity, exhibiting a melting point at 212°C and a heat of fusion of 6 J/g, as measured by DSC (see FIG. 3).

10

EXAMPLE IV

The pellets made by the procedure of Example I were injection molded to make preforms for a two-liter plastic bottle. A 150 ton Cincinnati/Milacron injection molder was used at a screw speed of 5000 rpm and temperatures of 277°C, 293°C, 299°C, and 310°C. The preforms formed at 310°C was clear, whereas the preforms made at 277°C was opaque and the other two were hazy.

15

EXAMPLE V

The clear preforms made at 310°C by the procedure of Example IV were thermo-blow molded into two-liter bottles using a Cincinnati/Milacron blow molding unit. The unit has a heating chamber through which the preform is drawn back and forth for a preset period of time; usually, this heating cycle lasts about 3 minutes. At the end of the heating cycle the preform is drawn out of the chamber and rotated for about 10-15 seconds (the equilibration cycle). Then a bottle mold closes around the preform and nitrogen gas is blown in and expands the preform to form a bottle; this blow cycle lasts about 7 seconds.

20

25

The preforms were blow molded under the following conditions: heating cycle of 3.40 minutes; equilibration of 15 seconds; heating temperature in the approximate range of 100-120°C.

FIG. 4 shows the results of a DSC analysis of a clear preform made according to Example IV, and FIGS. 5-6 show the DSC analyses of the neck and bottom portions, respectively, of a bottle blown therefrom. These results show that the preform and bottle both had a T_g of 87°C, a T_m of about 321°C, and a heat of fusion of about 24-25 J/g.

EXAMPLE VI

Melt extrusion was carried out on the same blend and with the same extruder as in Example I to compare pellets made at different temperatures and screw speeds. The results are shown in Table 1:

Table 1: Appearance of Pellets Extruded Under Different Conditions

Screw Speed (rpm)	Extruder Temperature (°C)		
	260	280	300
30	Opaque	Haze	Clear
120	-	Opaque	Opaque

FIG. 7 shows the results of three DSC analyses of the copolymer extruded at 260°C and 30 rpm. The first analysis showed a T_g of 80°C and two T_m 's at 245°C and 261°C, with a total heat of fusion of 37 J/g. The DSC heating continued to temperatures well above 300°C, which is believed to cause additional transesterification. Consequently, a reanalysis of the same material showed a T_g , T_m , and heat of fusion closer to that of the random copolymer (see FIG. 3). The

third analysis showed that the melting point and heat of fusion had become almost identical to that of the random copolymer. These results verify that additional heating of the copolymer produces a more random copolymer having a lower degree of crystallinity.

5 FIG. 8 shows the results of DSC analyses of the copolymers made at 300 C. The analysis of the copolymer extruded at 120 rpm (opaque pellets) is similar to the first analysis of the 260°C in regard to the T_g , T_m , and heat of fusion; a double melting point peak can be seen, although the two peaks are less distinct than in FIG. 7. The analysis of the copolymer extruded at 30 rpm (clear pellets) is
10 somewhat more similar to the second analysis of FIG. 7. These results provide evidence that the lower extrusion speed resulted in additional randomization (more transesterification) of the copolymer and reduced crystallinity. These results also suggest that if the extruder residence time, or melt mixing time, is sufficiently short, extrusion temperatures up to at least 300°C could be used in the practice of
15 the present invention; however, a temperature of about 260-280°C is preferred.

EXAMPLE VII

20 Four 20/80 PEN/PET blends were prepared using the polymers of Example I and a small Brabender mixer with a 70 g capacity to check the relationship between transesterification and mixing time and temperature. The polymers were melt mixed at two temperatures, 280°C and 300°C, for two different time periods, 3 and 5 minutes, at each temperature. The percent transesterification was measured by Fourier Transform NMR (using a 70/30 weight % mixture of
25 chloroform/trifluoroacetic acid) for each of the four copolymers so produced. The results are presented in Table 2:

Table 2: Effect of Melt Mixing Time and Temperature

Temp. (°C)	Time (min.)	% Transesterification
280	3	less than 15
280	5	17
300	3	20
300	5	57

The results in Table 2 show that the combination of high extrusion temperature (300°C) and long extruder residence time at that temperature (5 min) produces an undesirable amount of transesterification.

Many variations of the present invention not illustrated herein will occur to those skilled in the art. The present invention is not limited to the embodiments illustrated and described herein, but encompasses all the subject matter within the scope of the appended claims.

Claims

1. A process for making a transparent blow molded product made of a copolyester that does not thermally deform at temperatures below 85°C, said process comprising:

melt extruding about four parts by weight poly(ethylene terephthalate) together with one part by weight poly(ethylene naphthalene 2,6-dicarboxylate) at a temperature of from about 250°C to about 290°C for a time sufficient to produce about 1-20% transesterification of said polymers, to form a copolymer;

injection molding said copolymer at a temperature of from 290°C to about 320°C for no more than about three minutes to form a transparent preform in which said copolymer has a glass transition temperature of about 85-87°C or higher and has a melting point of 225°C or higher;

thermo-stretch blow molding said preform at a temperature between said glass transition temperature and the crystallization temperature of said copolymer to form a transparent product.

2. A transparent blow molded product made according to the process of claim 1.

3. The product set forth in claim 2 wherein the melting point of said copolymer is at least 230°C.

4. The product set forth in claim 2 wherein the heat of fusion of said copolymer is at least 20 J/g as measured by differential scanning calorimetry.

5. A process for making a transparent blow molded bottle made of a copolyester that does not thermally deform at temperatures below 85°C, said process comprising:

5 melt extruding about four parts by weight poly(ethylene terephthalate) together with one part by weight poly(ethylene naphthalene 2,6-dicarboxylate) at a temperature of from about 260°C to about 280°C for about 3-5 minutes, to form a copolymer;

10 injection molding said copolymer at a temperature of from 290°C to about 320°C for no more than three minutes to form a transparent preform in which said copolymer has a glass transition temperature of about 85-87°C or higher and has a melting point of 225°C or higher and a heat of fusion of at least about 20 J/g;

15 thermo-stretch blow molding said preform at a temperature in the approximate range of 100-120°C to form a transparent bottle.

6. A transparent bottle made according to the process of claim 5.

7. A process for making a transparent blow molded bottle made of a copolyester that does not thermally deform at temperatures below 85°C, said process comprising:

20 melt extruding about four parts by weight poly(ethylene terephthalate) together with one part by weight poly(ethylene naphthalene 2,6-dicarboxylate) at a temperature of from about 280°C to about 300°C for no longer than about 3 minutes, to form a copolymer;

25 injection molding said copolymer at a temperature of from 290°C to about 320°C for no more than about one minute to form a transparent preform in which said copolymer has a glass transition temperature of about

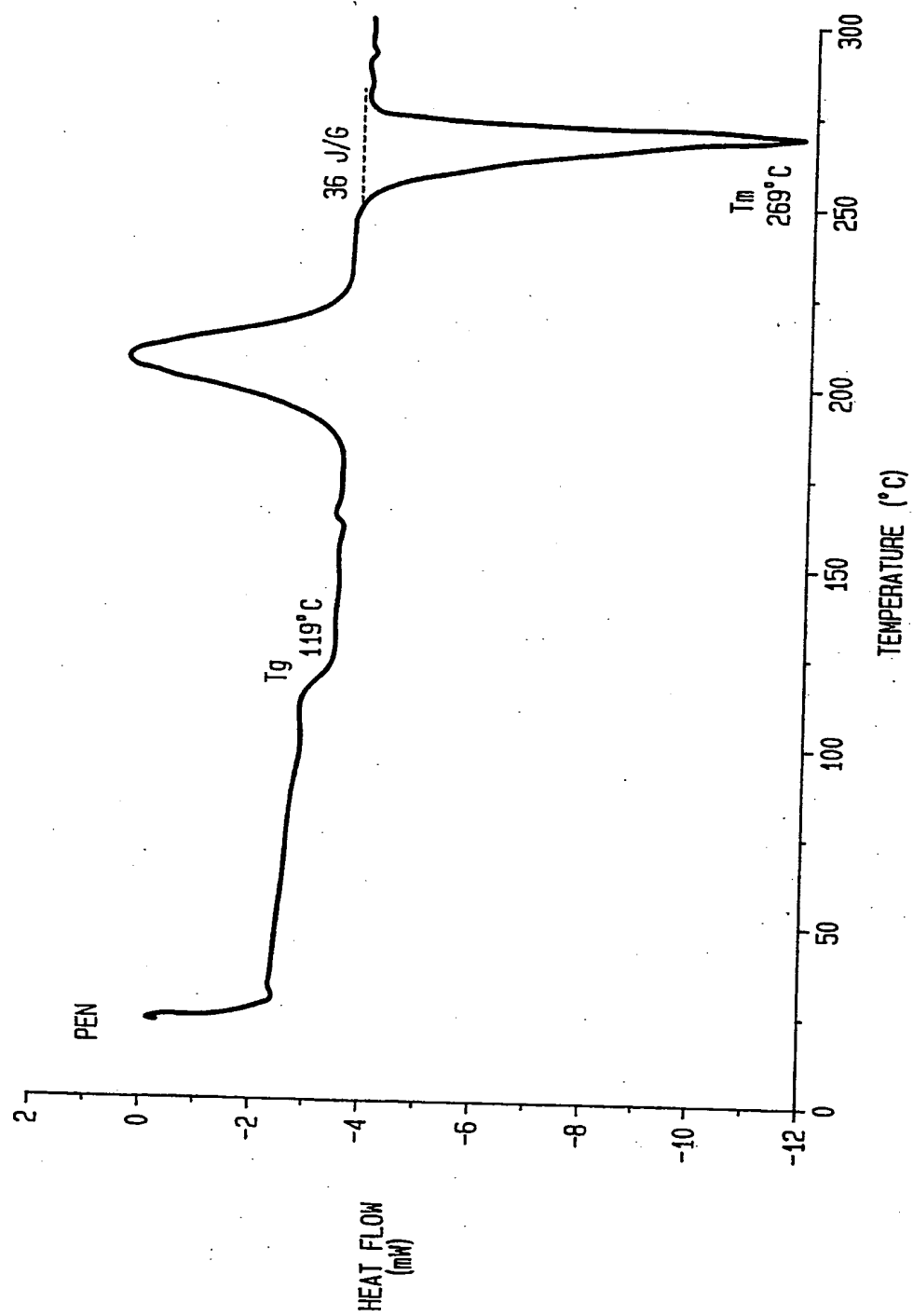
85-87°C or higher and has a melting point of 225°C or higher and a heat of fusion of at least about 20 J/g;

thermo-stretch blow molding said preform at a temperature in the approximate range of 100-120°C to form a transparent bottle.

- 5 8. A transparent bottle made according to the process of claim 7.

1/8

FIG. 1



2/8

FIG. 2

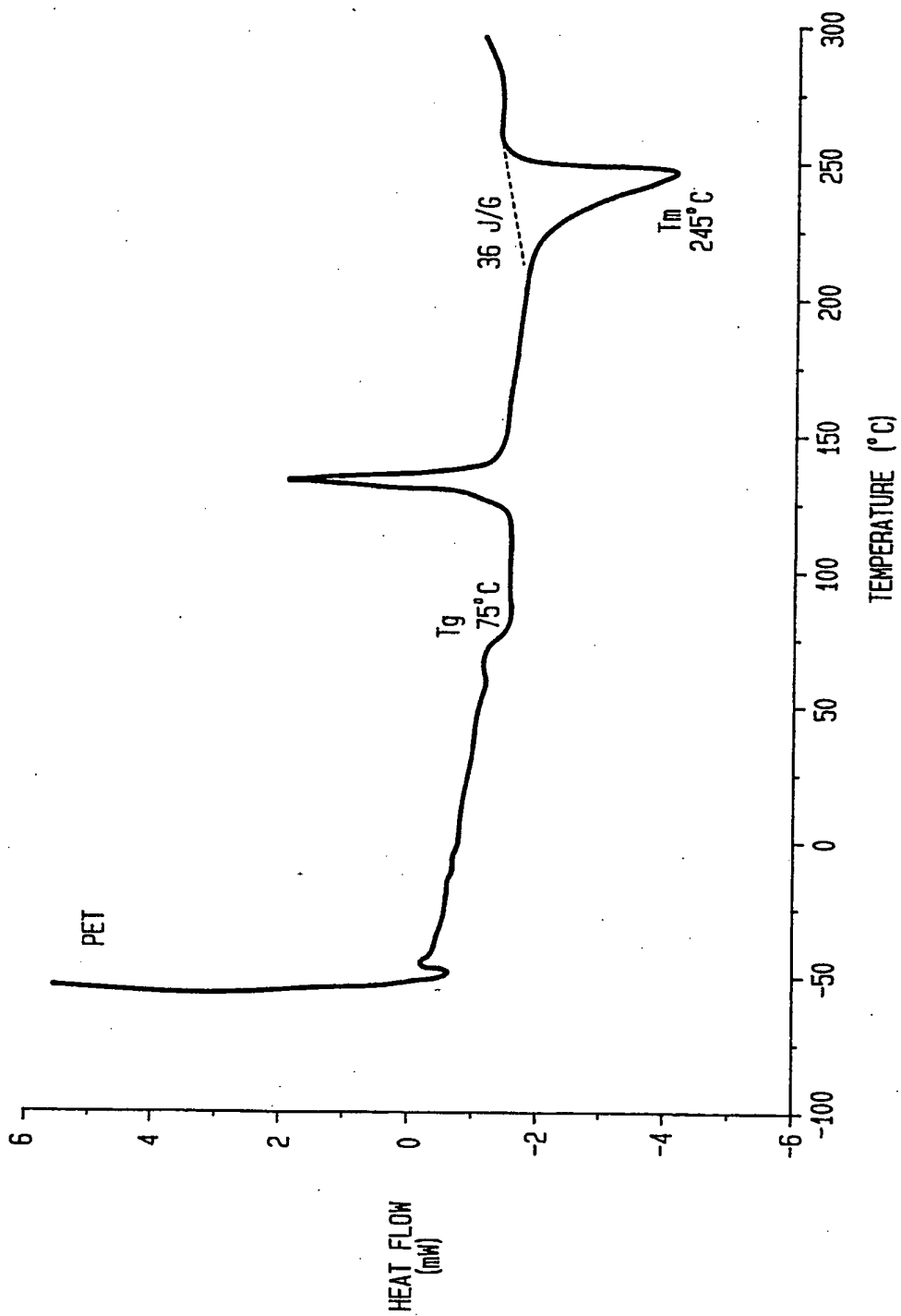


FIG. 3

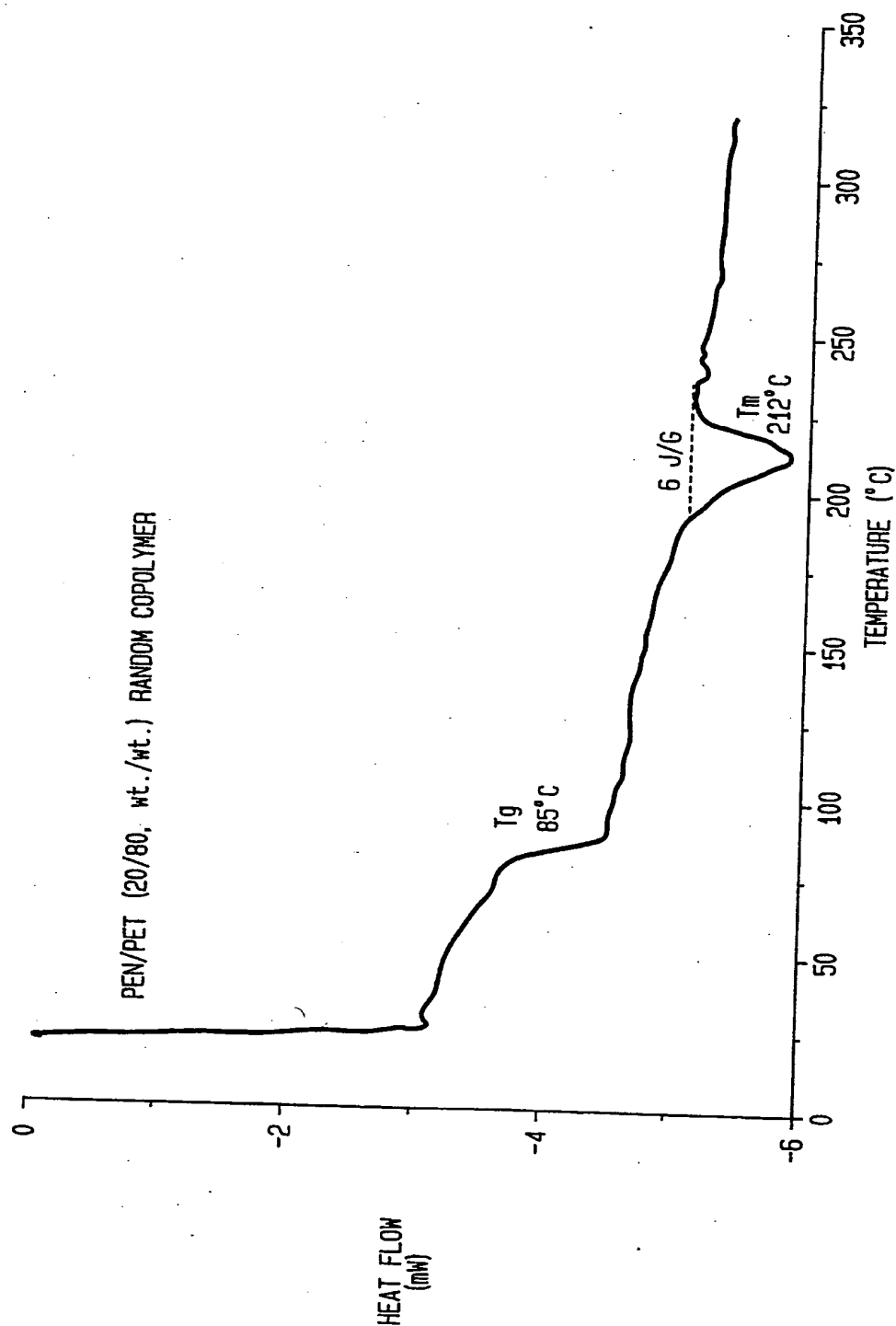
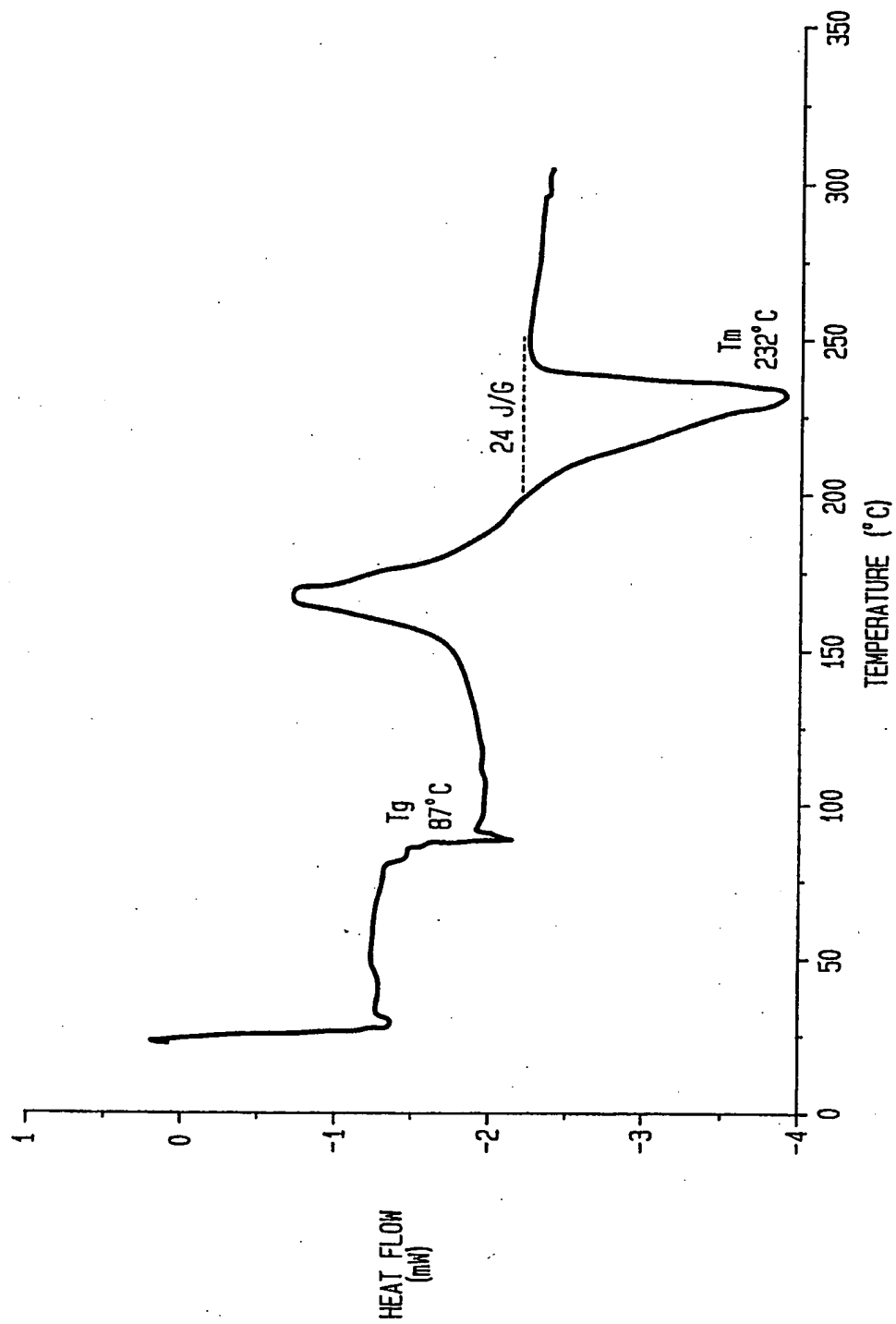
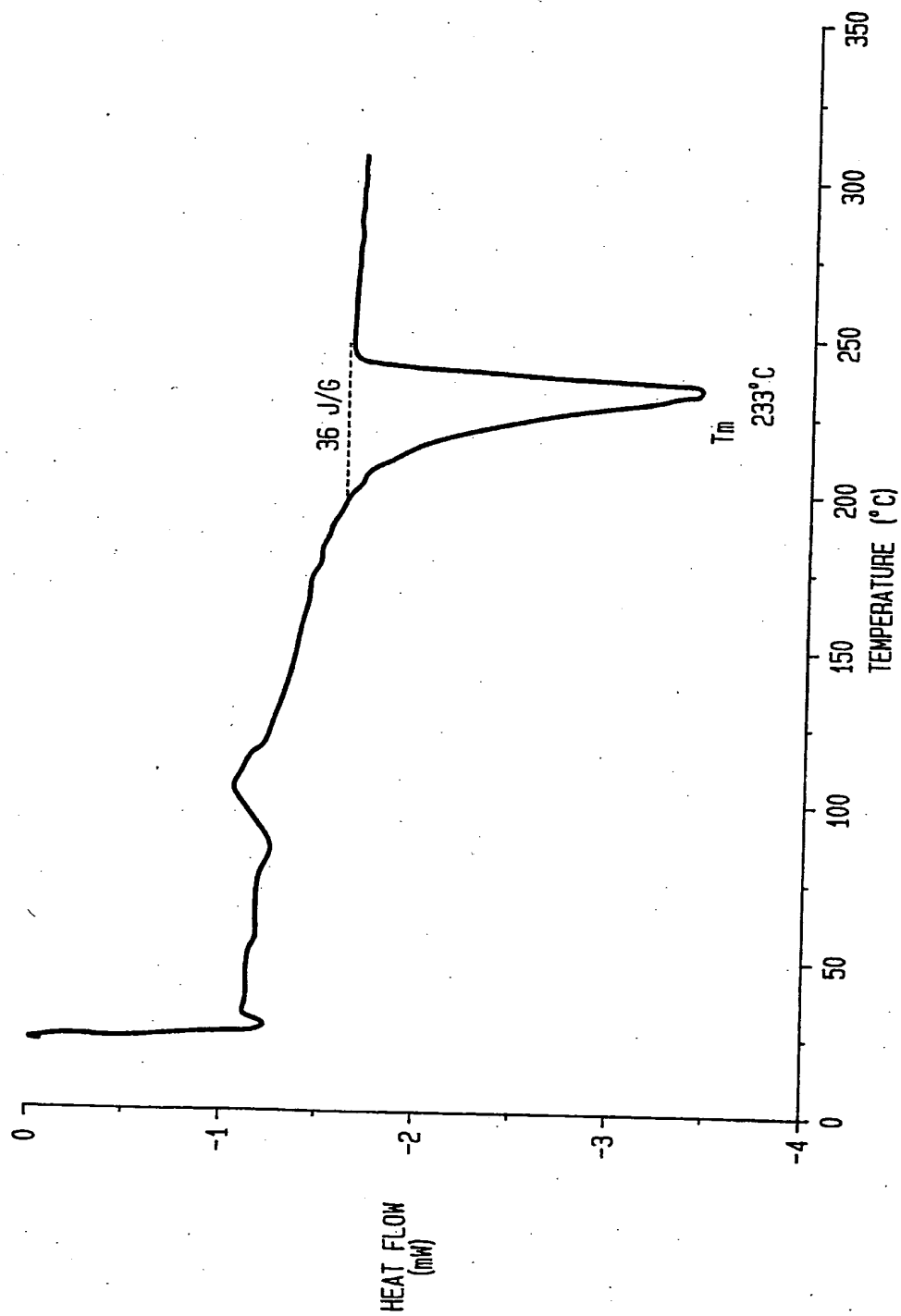


FIG. 4



5/8

FIG. 5



6/8

FIG. 6

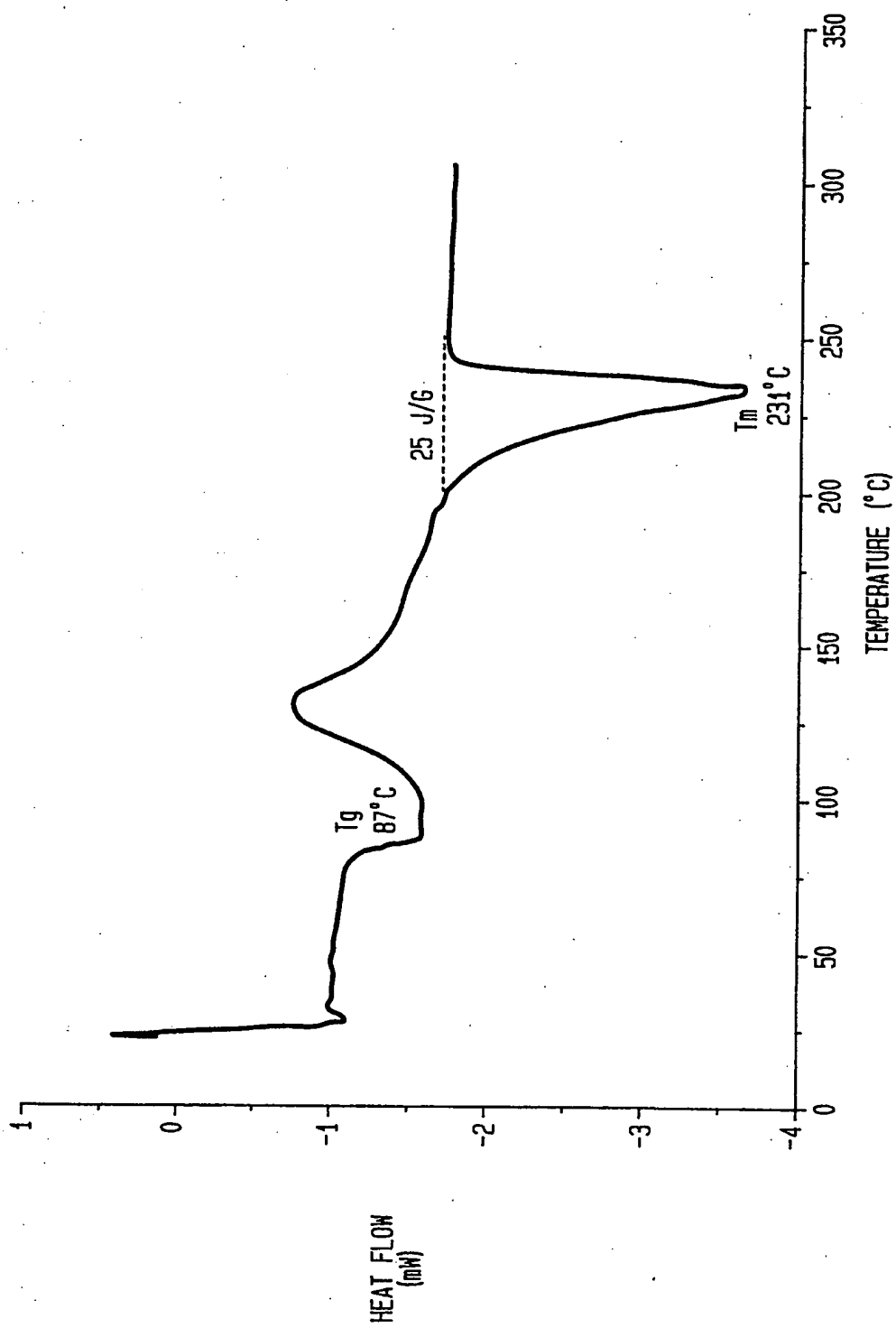
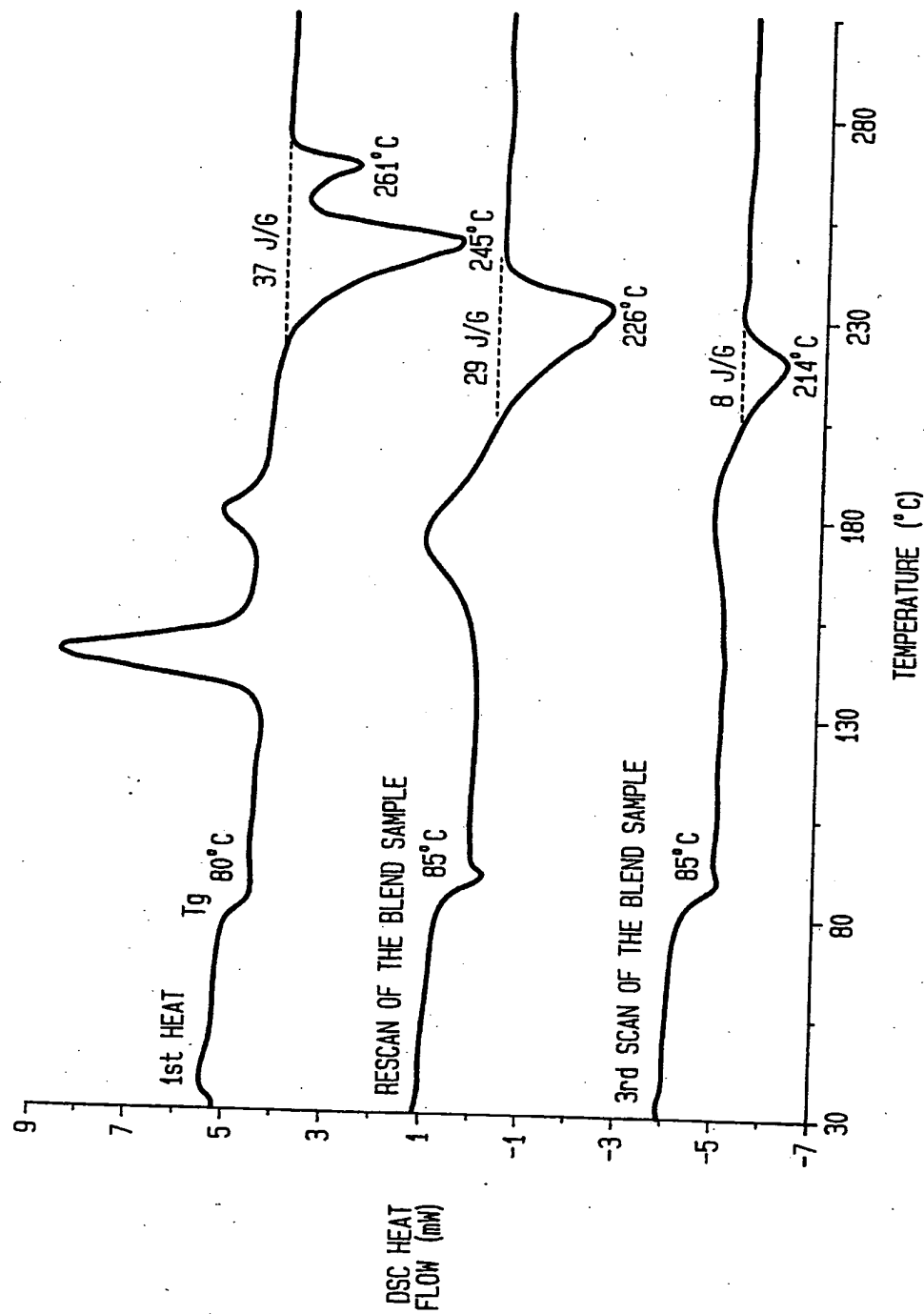
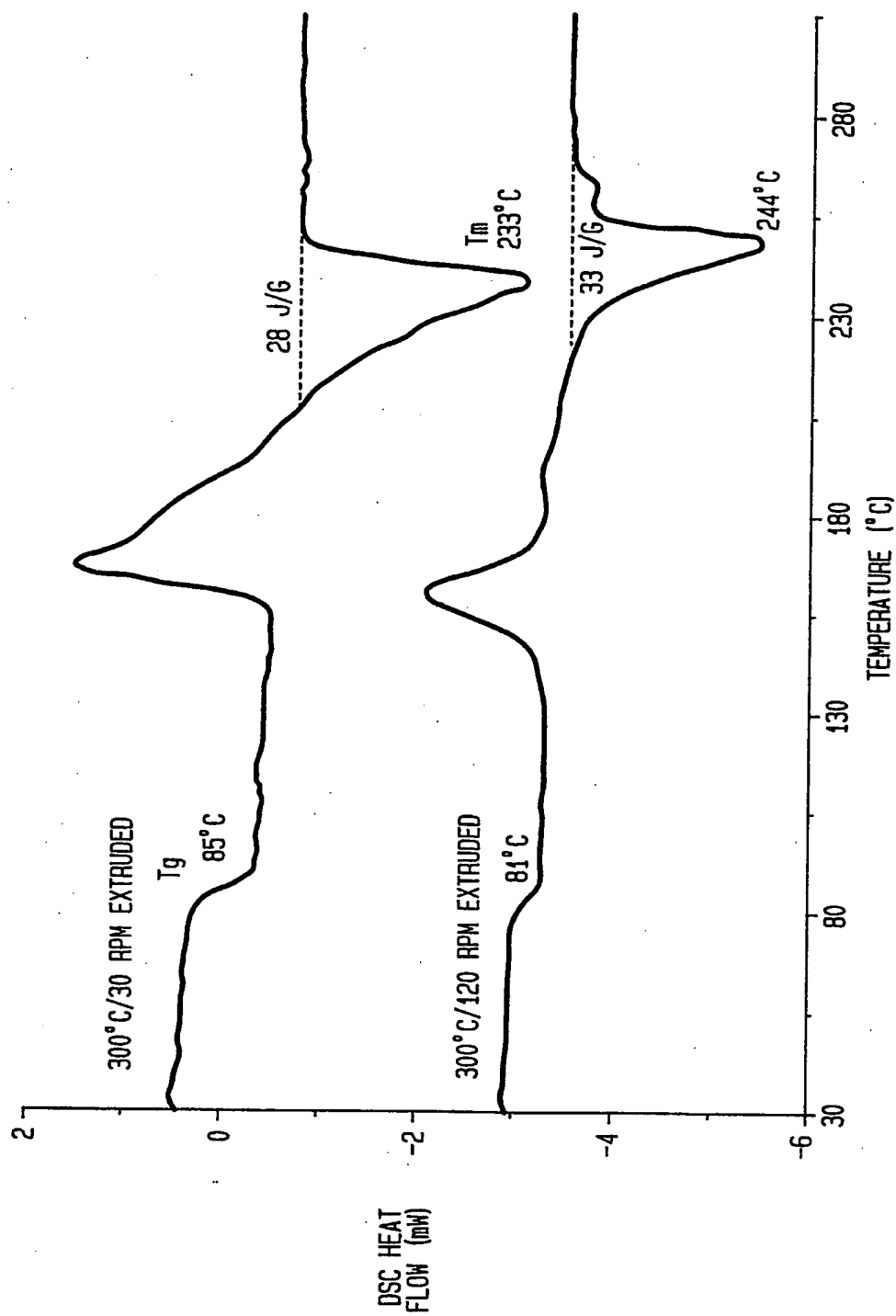


FIG. 7



8/8

FIG. 8



INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/03414

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B29C49/00 B29C67/24 C08L67/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B29C C08L C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 9241 Derwent Publications Ltd., London, GB; Class A23, AN 92-335782 XP002006281 & JP,A,04 239 624 (TEIJIN LTD) , 27 August 1992 see abstract	1-8
X	DATABASE WPI Section Ch, Week 9114 Derwent Publications Ltd., London, GB; Class A23, AN 91-098663 XP002006282 & JP,A,03 043 425 (TEIJIN KK) , 25 February 1991 see abstract	1-8

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *&* document member of the same patent family

Date of the actual completion of the international search

1 July 1996

Date of mailing of the international search report

15.07.1996

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Attalla, G

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/03414

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>PROCEEDINGS ANTEC 1993, vol. 2, 1993, NEW ORLEANS, pages 1222-1226, XP000573715 STEWART M. E. ET AL.: "Transesterification of poly(ethylene 2,6-naphthalene dicarboxylate)/poly(ethylene terephthalate) blends" cited in the application see page 1223, left-hand column, line 8 - line 27; figures 1,4</p> <p style="text-align: center;">---</p>	1-8
X	<p>RESEARCH DISCLOSURE, vol. 283, no. 040, November 1987, pages 680-684, XP002006279 cited in the application see example 2; table 4</p> <p style="text-align: center;">---</p>	1-8
A	<p>COLLOID AND POLYMER SCIENCE, vol. 272, no. 11, 1994, pages 1352-1362, XP000574275 ANDRESEN E. ET AL.: "Studies of miscibility, transesterification and crystallization in blends of poly(ethylene terephthalate) and poly(ethylene-2,6-naphthalene dicarboxylate)"</p> <p style="text-align: center;">---</p>	1-8
A	<p>US,A,5 006 613 (SHEPHERD FREDDIE A ET AL) 9 April 1991 cited in the application see examples 3,4</p> <p style="text-align: center;">---</p>	1-8
A	<p>DATABASE WPI Section Ch, Week 9241 Derwent Publications Ltd., London, GB; Class A23, AN 92-335783 XP002006283 & JP,A,04 239 625 (TEIJIN LTD) , 27 August 1992 see abstract</p> <p style="text-align: center;">-----</p>	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/03414

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5006613	09-04-91	NONE	